A

RESEARCH PROPOSAL

ON

SYNTHESIS AND CHARACTERIZATION OF THIN FILMS OF METAL (COPPER, INDIUM AND TIN) SELENIDES

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1. INTRODUCTION

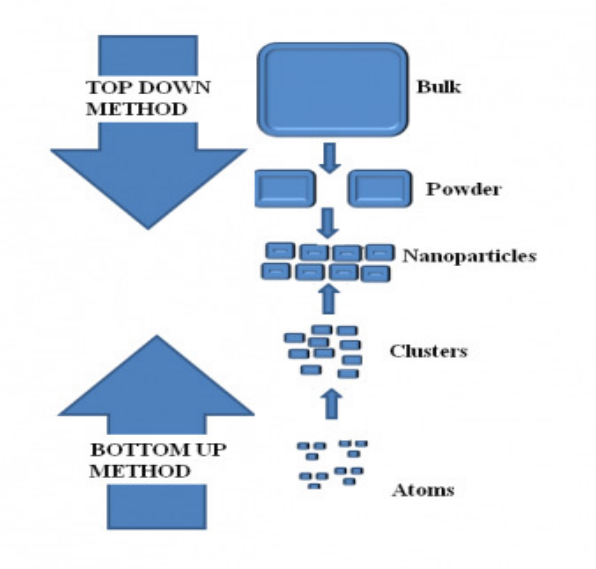
Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale Nanotechnologies are defined thus:

Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale.

Nanotechnology is the study and application of extremely small things and use of structures between 1 nanometer to 100 nanometer in size. The “nanoscale” is typically measured in nanometers, or billionths of a meter. At this scale, materials often exhibit distinctive physical and chemical properties due to quantum mechanical effects. Nanotechnology can be used across all other science fields such as Physics, Chemistry, and Biology. Nanotechnology also refers as manipulation of matter on an atomic, molecular or super molecular scale. In simple words it is defined as fabrication of device with atomic or molecular scale precision. Nanotechnology mainly consists of processing of separation, consolidation and deformation of material by one atom or by one molecule. Example of nanotechnology are: nanostructure catalyst, testing of nanosensor, new generation of lasers, quantum dots ,colloidal nanoparticle etc. There are two types of approaches for synthesis of nano material and fabrication of nano structure.

1. Top down
2. Bottom up

In the "Bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. E.g. nano-lithography. In the "Top-down" approach, nano-objects are constructed from larger entities without atomic-level control. Top down approach is practiced less as compared to the bottom up approach.



1.1 Approaches to Nanoscale Structures

Zero dimensional structures
In Zero dimensional nanostructure, Electrons are confined along all directions. The electrons are not allowed to move anywhere in the system. E.g. - Quantum dots, Nanoparticle.

One dimensional structure
In One dimensional Nanostructure, Electrons are confined in two dimensions. The electrons are allowed to move in only one direction in the system. E.g. - Nanotubes, Nanowires.

Two dimensional structures
In Two dimensional Nanostructures, Electrons are confined in only one direction. The electrons are allowed to move in any two directions in the system. E.g. - Thin films, Nanosheet

Three dimensional structures
In Three dimensional Nanostructures, Electrons are allowed to move in all the directions.
E.g. Nanodot.

1.2 Application of nanotechnology is as follows:

NANOTECHNOLOGY IN ENERGY SECTOR: Nanotechnology can also benefit the energy sector. The development of more effective energy-producing, energy-absorbing, and energy storage products in smaller and more efficient devices is possible with this technology. Such items like batteries, fuel cells, and solar cells can be built smaller but can be made to be more effective with this technology.

NANOTECHNOLOGY IN DRUGS: In the medical world, nanotechnology can also be seen as a boon since these can help with creating smart drugs. These help cure people faster and without the side effects that other traditional drugs have.

SOLAR CELL: Companies have developed nanotech solar cells that can be manufactured at significantly lower cost than conventional solar cells.

FUEL CELLS: Nanotechnology is being used to reduce the cost of catalysts used in fuel cells to produce hydrogen ions from fuel such as methanol and to improve the efficiency of membranes used in fuel cells to separate hydrogen ions from other gases such as oxygen.

FABRIC: Making composite fabric with nano-sized particles or fibers allows improvement of fabric properties without a significant increase in weight, thickness, or stiffness.

CHEMICAL SENSOR: Nanotechnology can enable sensors to detect very small amounts of chemical vapors. Various types of detecting elements, such as carbon Nanotubes, zinc oxide Nanowires or palladium nanoparticle can be used in nanotechnology-based sensors.

1.3 THIN FILM

Thin film deposition is the technology of applying very thin film of material – between a few nanometers to about 100 micrometers , or the thickness of few atoms – onto a substrate surface to be coated ,or onto a previously deposited coating to form layers . Thin film deposition is divided into two categories - chemical deposition and physical vapor deposition coating system.

Chemical deposition is when a volatile fluid precursor produces a chemical change on a surface leaving a chemically deposited coating. One example is chemical vapor deposition used to produce the highest purity, highest – performance solid materials in the semiconductor industry.

Physical vapor deposition refers to a wide range of technologies where material is released from a source and deposited on a substrate using mechanical or thermodynamic processes. Physical method covers the deposition techniques which depend on the evaporation or ejection of the material from a source, i.e. evaporation or sputtering. The two most common techniques of physical vapor deposition or PVD are Thermal evaporation and sputtering.

Thin film materials have been widely used in semiconductor devices, wireless communications, telecommunications, integrated circuits, rectifiers, transistors, solar cells, light-emitting diodes, photoconductors, light crystal displays, magneto-optic memories, audio and video systems, compact discs, electro-optic coatings, memories, multilayer capacitors, flat-panel displays, smart windows, computer chips, , lithography, micro electromechanical systems (MEMS), and multifunctional emerging coatings, as well as other emerging cutting technologies.

Thin-film photovoltaic cells

Thin-film technologies are also being developed as a means of substantially reducing the cost of solar cells. Thin film solar cells are cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs. This is especially represented in the use of printed electronics processes

Thin-film batteries

Thin-film printing technology is being used to apply solid-state lithium polymers to a variety of substrates to create unique batteries for specialized applications. Thin-film batteries can be deposited directly onto chips or chip packages in any shape or size. Flexible batteries can be made by printing onto plastic, thin metal foil, or paper.

Electrically operating coatings

Thin layers from elemental metals like copper, aluminum, gold or silver etc. and alloys have found numerous applications in electrical devices. Due to their high electrical conductivity they are able to transport electrical currents or supply voltages.

Selenide is a chemical compound containing a Selenium anion with oxidation number of −2 (Se^{2-}), much as Sulfur does in a Sulfide. Some Selenides are reactive to oxidation by air. Metal Selenides are more easily decomposed to the elements than are Sulfides. Selenides of electropositive metals: such as Aluminium Selenide readily hydrolyse, even in moist air, evolving toxic hydrogen Selenide gas. Pure Selenide minerals are rare; instead Selenium tends to partially substitute for sulfide in many sulfide minerals.

Indium Selenide

Indium Selenide is a compound of indium and selenium having melting point 890^{O}C .It has potential for use in photovoltaic device. The two most common phases α and β have a layered structure, while γ is a defect wurtzite structure. The crystalline form of a sample can depend on the method of production, for example thin films of pure γ-In_2Se_3 have been produced from trimethylindium**.** Indium Selenide is a semiconducting compound of the III-VI type that crystallizes in a lattice structure. Copper Indium Selenide -based technology provides the most efficient solar energy conversion among all thin-film photovoltaic devices.

Copper Selenide

Copper Selenide is an inorganic binary compound consisting of Copper and Selenium. Its formula is sometimes described as CuSe or Cu_2Se, but it is non-stoichiometric. It is a semiconductor and is frequently grown as nanoparticle or other nanostructures. Copper Selenide having melting point 1113^{o}C.Copper Selenide is a thermoelectric material used in number of industrial applications including infrared detection and imaging. It has also been investigated for use in treatment of colon cancer.

Tin Selenide

Tin Selenide also known as stannous Selenide, is an inorganic compound with the formula (SnSe), where Tin has a +2 oxidation state. Tin Selenide is a narrow band-gap (IV-VI) semiconductor and had been used for applications including low-cost photovoltaics and memory-switching devices. Tin Selenide is a typical layered metal chalcogenide, it includes a Group 16 anion (Se^{2-}) and an electropositive element (Sn^{2+}), and it is arranged in a layered structure.

Tin Selenide exhibits low thermal conductivity as well as reasonable electrical conductivity, creating the possibility of it being used in thermoelectric materials. Tin Selenide (SnSe) having stiff bonds and distorted lattice. Tin Selenide can be formed by reacting the elements tin and selenium above 350 °C. It having melting point 861^{o}C

Tin Selenides may be used for optoelectronic devices, solar cells, memory switching devices, and anodes for lithium-ion batteries. Tin Selenide has an additional use as a solid-state lubricant, due to the nature of its interlayer bonding. So, it is not the most stable of the chalcogenide solid-state lubricants, as tungsten di-Selenide has much weaker interplanar bonding, is highly chemically inert and has high stability in high-temperature, high-vacuum environments.

2. REVIEW OF LITERATURE

1. **Issac** et al. (2018) reported that Thermal evaporation was utilized to deposit Copper Selenide thin films at different substrate temperatures (T_S). Impact of substrate temperature on film structure, morphology, optical and electrical properties was investigated. Structural transformation from orthorhombic to cubic phase with different stoichiometric compositions was evident upon an increase in substrate temperature. The Film morphology demonstrates various shapes from scattered grains to columnar crystals upon heat treatment. The optical analysis illustrates strong absorption in the blue region and the band gap values lies in the range 1.54ev-2.54 eV. The electrical resistivity was found to be in the order of 10^{-4} Ωcm.

2. **Ahad** et al. (2018) reported that Copper Selenide film electrodes prepared by combined electrochemical (ECD) followed by chemical bath deposition (CBD), may yield high photo electrochemical conversion efficiency (~14.6%) with no further treatment. The new ECD/ CBD Copper Selenide film electrodes show enhanced PEC characteristics and exhibit high stability under PEC conditions, compared to the ECD or the CBD films deposited separately. The electrodes combine the advantages of both ECD – Copper Selenide electrodes (in terms of good adherence to FTO surface and high surface uniformity) and CBD-copper Selenide electrodes (suitable film thickness). Effect of annealing temperature, on the ECD/CBD film electrode composition and efficiency, was discussed.

3. **Bindu** et al. (2018) prepared Single phase polycrystalline Sn-doped $CuInO_2$ thin films by the oxygen plasma enhanced reactive evaporation method. X-ray diffraction indicated a preferential orientation of crystallites along the (006) plane on doping while energy dispersive analysis of X-rays and atomic force microscopy were employed to appraise the composition and morphology of the films, respectively. Remarkably, about 2-3 orders of magnitude enhancement in their electrical conductivity than that reported were observed. Further, the Sn-doped thin films possessed 2-3 orders of magnitude higher carrier concentration (10^{18}-10^{19}/cm^3) than undoped films that were associated with a drastic reduction in mobility. Moreover, different conduction mechanisms possible at different temperature regions ranging from around 55 K–450 K were studied in detail. While the transparency of the films was observed to increase from 43% to 85% on doping, the optical band gap decreased from 3.83 eV to 3.5 eV.

4. **Razykov** et al. (2018) fabricated the thin film of SnSe first time by chemical molecular beam deposition (CMBD) in atmospheric pressure hydrogen flow using polycrystalline Tin Selenium (SnSe) precursors. The morphological and electrical properties of the films were studied as a function of the precursor's composition and the substrate temperature. Experimental data indicate that in the resulting thin films Se enrichment takes place at low substrate temperatures, despite the different compositions of the SnSe precursor during the synthesis. In this case, the grain sizes of the films vary in the range of (8–20) μm, depending on the substrate temperature. In addition, X-ray diffraction analysis of the samples shows that the films have an orthorhombic crystalline structure. The electrical conductivity of films measured varies between 6 and 90 $(\Omega \times cm)^{-1}$. The optical measurements on selected SnSe thin films illustrate that the samples have an optical bandgap of (1.1–1.2) eV and the absorption coefficient of $\sim 105\ cm^{-1}$, which is suitable for thin film solar cells.

5. **Howell** et al. (2018) reported that Tin Selenide as an attractive material for photovoltaic devices as an absorber layer. There are two derivatives: SnSe and $SnSe_2$. SnSe is a p-type material that exhibits a band gap of 1.0 eV. $SnSe_2$ is a n-type material with a band gap of 1.6 eV. They studied, Tin Selenide thin films have been electrochemically deposited using a process known as electrochemical atomic layer deposition (E-ALD). E-ALD uses the phenomenon known as under potential deposition to deposit an atomic monolayer of each element separately. This process was known as a cycle and repeated until the desired thickness was achieved. These films need further optimization for the selection of one species over the other. Initial photolectrochemical studies have shown the current thin film is p-type and was an option for a photocathode for hydrogen production in a photolectrochemical cell. Further studies will include improving the deposition cycle used to increase the photo response of the material and to gain control over the appearance of SnSe or $SnSe_2$.

6. **Boolchandani** et al. (2018) studied that indium selenium (InSe) bilayer thin films of various thickness ratios, $In_xSe_{(1-x)}$ (x = 0.25, 0.50, 0.75), were deposited on a glass substrate keeping overall the same thickness of 2500 Å using thermal evaporation method under high vacuum atmosphere. Electrical, optical, and structural properties of these bilayer thin films have been compared before and after thermal annealing at different temperatures. The structural and morphological characterization was done using XRD and SEM, respectively. The optical bandgap of these thin films has been calculated by Tauc's relation that varies within the range of 1.99 to 2.05 eV. A simple low-cost thermoelectrical power measurement setup is designed which can measure the Seebeck coefficient "S" in the vacuum with temperature variation. The setup temperature variation was up to 70°C. Also, they studied that the thermoelectric power of Indium Selenide (InSe) and Aluminum Selenide (AlSe) bilayer thin films prepared and annealed

in the same way was calculated. The thermoelectric power has been measured by estimating the Seebeck coefficient for InSe and AlSe bilayer thin films. It was observed that the Seebeck coefficient is negative for InSe and AlSe thin films.

7. **Posada** et al. (2018) reported that this work explores a strategy to bring together the advantages of co-evaporation and sputtering by developing a hybrid co-sputtering/evaporation process, where copper, indium, and gallium are sputtered with the thermal evaporation of selenium. A 3-stage hybrid co-sputtering/evaporation process for Cu (In,Ga) Se_2 (CIGS) thin films solar cells have been developed by controlling the deposition parameters (temperature, sputtering power, and evaporation). (In, Ga) $_2Se_3$ layers are deposited in the first stage, followed by $Cu_{2-x}Se$ and $Cu_{2-x}Se$/ $(In,Ga)_2Se_3$ layers. Material properties at different steps were studied in detail by X-ray fluorescence, energy dispersive X-ray, scanning electron microscopy, glow discharge optical emission spectroscopy, Raman spectroscopy, and X-ray diffraction. Solar cells were completed leading to 9.7% efficiency.

8. **Taha** et al. (2018) studied that indium Tin Oxide (ITO) and Silver doped ITO thin films at different Ag concentrations (2, 4, 6 and 10 atomic %) were fabricated by a sol-gel spin coating technique. The thin film coatings were post annealed at 500 °C. Structural, mechanical, surface morphology, electrical and optical characteristics of the ITO and Ag-doped ITO thin films were studied as a function of Ag concentrations. XRD results are consistent with the presence of body centered cubic structure of the indium oxide polycrystalline phase with a new peak for Ag at $2\theta \approx 38.2°$, indicating that by introducing Ag atoms they do not remarkably change the structural characteristics of the ITO films. FESEM images display the formation of ITO and Ag-doped ITO nanoparticle and the average crystallite size increases after annealing treatment as well as the incorporation of Ag concentration. The observed improvement in **E** and **H** is 14% and 28% respectively, with the hardness and Young's modulus finally reaching 6.7 GPa and 148 GPa, respectively. Loading carrying capability and wear resistance are also enhanced by doping and annealing treatment. After annealing at 500 °C, the thin film coatings with the electrical resistivity of $2.4 \times 10^{-4}\ \Omega\,\text{cm}$, carrier concentration of $6.8 \times 10^{20}\ \text{cm}^{-3}$ and carrier mobility of $37\ \text{cm}^2/\text{V s}$ were achieved when the Ag doping level was 4 at %. On the other hand, the maximum optical transparency was found to be 92% for both ITO and 2% Ag-doped ITO thin films after being annealed at 500 °C. The variation of optical constants, such as absorption coefficient, refractive index and extinction coefficient with different Ag concentrations, were also studied.

9. **Lin** et al.(2017) reported that a solid-state thermoelectric device are attractive for diverse technological areas such as cooling, power generation and waste heat recovery with unique advantages of quiet operation, zero hazardous emissions, and long lifetime. With the rapid growth of flexible electronics and miniature sensors, the low-cost flexible thermoelectric energy harvester is highly desired as a potential power supply. Here in, a flexible thermoelectric Copper Selenide (Cu_2Se) thin film, consisting of earth-abundant elements, is reported. The thin film was fabricated by a low-cost and scalable spin coating process using ink solution with a truly soluble precursor. The Cu_2Se thin film exhibits a power factor of 0.62 mW/(m K^2) at 684 K on rigid Al_2O_3 substrate and 0.46 mW/(m K^2) at 664 K on flexible polyimide substrate, which was much higher than the values obtained from other solution processed Cu_2Se thin films (<0.1 mW/(m K^2)) and among the highest values reported in all flexible thermoelectric films to date (≈0.5 mW/(m K^2)). Additionally, the fabricated thin film shows great promise to be integrated with the flexible electronic devices, with negligible performance change after 1000 bending cycles. Together, the study demonstrates a low-cost and scalable pathway to high-performance flexible thin film thermoelectric devices from relatively earth-abundant elements.

10. **Matur** et al. (2017) studied that well crystallized Copper Indium Gallium (di)Selenide-$Cu(In,Ga)Se_2$ (CIGS) thin films were deposited on conducting substrates (molybdenum coated soda-lime glass) by sol–gel dip coating technique. The n-type Cadmium Sulfide (CdS) buffer layers were produced by chemical bath deposition (CBD) technique and the n-type ZnO: Al thin film has been used as transparent conductive layer was deposited by sol–gel dip coating technique. The selenium powder were dissolved in trioctylphosphine (TOP, 90%, technical grade) solution during the experiment process to make some progress on scientific innovation of CIGS thin films derived by sol–gel dip coating technique. The structural, optical and current–voltage (*I*–*V*) characteristics of the CIGS based heterojunction were analyzed by using the SLSG/Mo/CIGS/CdS/ZnO:Al/Al device configuration. The optoelectronic properties such as the open-circuit voltage (V_{oc}), the short-circuit current (I_{sc}), the fill factor (FF), the ideality factor (*n*) etc. of the CIGS thin film solar cells were examined depending on the annealing temperature at 500 °C for 45 minutes in air. The CIGS thin film heterojunction which has been obtained present diode like rectifying behavior besides photovoltaic behavior under UV illumination.

11. **Goon** et al. (2016) reported that the method of fabricating a CIGS thin film for solar cells using a simplified co-vacuum evaporation process and a CIGS thin film fabricated by the method are disclosed. The method includes: (a) depositing Cu, Ga and Se on a substrate having a substrate temperature ranging from 500° C. to 600° C. through co-vacuum evaporation, (b) depositing Cu,

Ga, Se and In through co-vacuum evaporation while maintaining the same substrate temperature as in step (a), and (c) depositing Ga and Se through co-vacuum evaporation, followed by depositing Se alone through vacuum evaporation while lowering the temperature of the substrate. The method can realize crystal growth and band-gap grading by Ga composition distribution while simplifying process steps and significantly reducing a film-deposition time, as compared with a conventional co-vacuum evaporation process, thereby providing improvement in process efficiency.

12. **Soundararajan** et al. (2015) reported that Copper Selenide (CuSe) thin films were prepared by chemical bath deposition (CBD) method. The structural and the morphological properties of CuSe thin films were investigated by XRD and SEM methods. The XRD studies showed well crystallized and cubic structure of CuSe thin films. The UV-Visible transmission spectrum showed excellent transmission in the entire visible region. The dielectric properties of the synthesized CuSe thin films were studied at different frequencies and different temperatures. They found that AC electrical conductivity increase with an increase in the temperature and the frequency. The activation energy was found to be 0.032 eV. The temperature dependent conductivity indicated the exponential behavior of the temperature dependent current confirming the semiconducting nature of the thin films.

13. **Ashaq** et al. (2014) reported that micro sized particles of Indium Tin Oxide (ITO) were reduced to nanosized particles through a simple reaction of indium Tin Oxide (ITO) and de-ionized water at 210^{O}C. The typical average diameters of as –grown nanoparticle were 80 nm to 110 nm. The phase purity and morphology of the products were characterized by x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscope (TEM). The possible mechanism of formation of ITO nanoparticles was proposed in brief through mathematical model.

14. **Ramesh** et al. (2014) reported that thin films of Copper Selenide had been deposited on Indium Doped Tin Oxide coated glass substrates. X-ray diffraction analysis revealed that the deposited films possess polycrystalline in nature. Optical absorption analysis showed that the deposited films possess band gap value around 2.1 eV.

15. **Man Xu** et al.(2014) reported that a systematic study of the effect of variation of the Zinc Oxide (ZnO) and Copper Indium Gallium (di)Selenide (CIGS) layer thickness on the absorption characteristics of CIGS solar cells using a simulation program based on finite element method (FEM). They show that the absorption in the CIGS layer does not decrease monotonically with its layer thickness due to interference effects. High precision is required in the CIGS production process, especially when using ultra-thin absorber layers, to accurately realize the required thickness of the ZnO, Cadmium Sulfide (CdS) and CIGS layer. They showed that patterning the ZnO window layer can strongly suppress these interference effects allowing a higher tolerance in the production process.

16. **Nordin** et al.(2014)proposed that Tin Selenide (SnSe) and Copper Indium Diselenide ($CuInSe_2$) compounds were synthesized by high temperature reaction method using combination of sealed ampoule (at relatively low pressure ~10^{-1} Pa without inert gas) and heating at specific temperature profile in rocking furnace. Powder X-Ray diffraction analysis showed that the products involved only single phases of SnSe and of $CuInSe_2$ only. Using the reaction products as source materials, the SnSe and $CuInSe_2$ thin films were vacuum-deposited on glass substrates at room temperature. Structural, elemental, surface morphological and optical properties of the as-deposited films were studied by X-Ray diffraction (XRD), energy dispersive X-Ray (EDX) analysis, field emission scanning electron microscopy (FESEM) and UV-Vis-NIR spectroscopy. Single phase of SnSe and $CuInSe_2$ films were obtained by thermal evaporation technique from synthesized SnSe and $CuInSe_2$ compound without further treatment.

17. **Ezenwa** et al. (2013) reported the synthesis of CuSe thin film by chemical bath deposition. A bandgap of 2.2eV were obtained for CuSe thin film. Refractive index of approximately 2.5 was obtained for CuSe thin film throughout the UV/VIS/NIR region of the electromagnetic spectrum. The film with the highest concentration has the highest absorbance, with a value of **> 0.6,** and the lowest transmittance of approximately 20% throughout the UV/VIS/NIR region of the electromagnetic. The film with the lowest concentration has the lowest absorbance, with a value of **> 0.1,** and the highest transmittance of approximately 90% throughout the UV/VIS/NIR region of the electromagnetic.

18. **Kumar** et al.(2012) reported that Tin Selenide (SnSe) thin films were prepared from the pulverized compound material by thermal evaporation method, to study the effect of film thickness on its structural, and optical properties. Tin Selenide thin films had been successfully grown by thermal evaporation method on glass substrates held at room temperature with varying the film thicknesses from 150 nm to 500 nm. The structural analysis suggests that the

thin films were polycrystalline in nature having preferred orientation in (111) direction. The electrical resistivity shows that the films were semi-conducting in behavior having p-type conductivity. The direct energy band gap calculated from the transmission data were in the range 1.74 to 1.24 eV. The electrical data shows that the SnSe thin film indicating semi-conducting behavior with p-type conductivity. The narrow optical band gap (~1.3 eV) having p-type conductivity indicates its use in photovoltaic applications

19. **Chaudhari** et al.(2011) reported that Thin films having different thickness of InSe were deposited by thermal evaporation technique, onto precleaned amorphous glass substrate. The structural properties of films were evaluated by XRD, optical microscopy and TEM. The X-ray diffraction analysis confirms that films are polycrystalline having cubic structure cell. The average grain size is found to be 11.18 -11.93 nm. The optical band gaps of the films were measured by using optical absorption spectra. The estimated values of the direct and indirect optical band gaps of these samples were 0.81 to 0.84 eV and 1.31 to 2.18 eV respectively.

20. Marcela et al. (2011) proposed that direct mechanochemical synthesis of Tin Selenide and Tin Selenide/Tin Diselenide composite from Tin and Selenium elements by high-energy milling was a very simple room temperature process with relatively short reaction time. X-ray diffraction and TEM analyses have shown that SnSe occurs in orthorhombic modification, whereas in the $SnSe/SnSe_2$ composite orthorhombic SnSe and hexagonal $SnSe_2$ coexist. Selenide crystals range from a few nanometers up to 100 nm in size, and they form agglomerated clusters. UV-Vis optical absorption spectrophotometry did not indicate a quantum confinement effect because the particle sizes of both synthesized compounds were larger than the excitonic Bohr radius of the bulk SnSe or $SnSe/SnSe_2$.

21. **Guanjun** et al. (2011) reported that they developed a one-pot solution strategy to synthesize Copper Selenide Nanocrystals with controllable shape and structure. By changing the precursors in the reaction, Copper Selenide Nanocrystals (nanorods and CuSe nanoplates) with various morphologies could be achieved. They proposed a possible mechanism to explain the influence of precursors on the shape of Copper Selenide Nanocrystals and found that the chemical activities of precursors played key roles in the morphologies and crystal structures of the final products. Moreover, the electrical transport properties of as-prepared products were investigated. The morphologies of Copper Selenide Nanocrystals have a great influence on the electrical transport properties. The Copper Selenide NCs with nanorods display the best electrochemical performance compared with the other two types. They believe that Copper Selenide Nanocrystals are best for electrical transport.

22. **PRABAHAR** et al. (2010) studied that Structural properties of Copper Indium Diselenide thin film measured by using high purity elemental Cu, In and Se taken according to their weight percentage. The $CuInSe_2$ compounds were found to exhibit Chalcopyrite structure.$CuInSe_2$ thin films of different thicknesses have been deposited on well cleaned glass substrates by thermal evaporation technique. The films were found to be polycrystalline in nature, 50 single phase exhibiting chalcopyrite structure. The crystallites having preferred orientation along the (112) direction. As the Substrate temperature increases the films were found to exhibit a highly preferred orientation along the (112) direction like a single crystal. The SEM micrograph of the deposited $CuInSe_2$ films confirms the crystalline nature of the films.

23. **Indirajith** et al. (2010) reported that Tin Selenide alloy were synthesized by following simple chemical reaction method, at comparatively lower temperature of 100 °C, from alkaline medium using SnCl2.2H2O and Selenium as source materials. Powder X-ray diffraction analysis reveals that the particle size of the synthesized product is in nanometer scale. Using the reaction product as source material, the SnSe films were deposited on glass substrates at room temperature, 150 °C, 250 °C, 350 °C and 450 °C. Structural, elemental, optical, surface morphological and electrical properties of the as deposited films were studied by X-ray diffraction, Energy Dispersive X-ray Analysis, UV-Vis-NIR, Scanning Electron Microscopy and Hall Effect measurement techniques and the relevant details had been obtained.

RESEARCH GAP

Copper Selenide, Indium Selenide and Tin Selenide have narrow band gap, suitable for various optoelectronic applications like memory switching devices, photovoltaic, light emitting devices (LED), and holographic recording systems. Due to large availability of constituents of these compounds in nature has been raised attention for the cost effective solution in photovoltaic applications. The structure of these materials thin films strongly influences the optical and electrical properties, which is dependent on the preparation technique. So by changing proportion of compound and structure there will be change in bandgap and modification in electrical properties. This can be used in betterment of commercial solar cell.

4. MOTIVATION

Nano dots based on metal Selenides have been extensively used for their distinctive spectral properties. Copper Selenide is a thermoelectric material used in a number of industrial applications including infrared detection and imaging. Indium Selenide -based technology provides the most efficient solar energy conversion among all thin-film photovoltaic devices. Tin Selenides used for optoelectronic devices, solar cells, memory switching devices, and anodes for lithium-ion batteries.

5. OBJECTIVES

1. To prepare thin films of Copper Selenide, Indium Selenide and Tin Selenide by thermal evaporation method.
2. To prepare thin films of composite of Copper Selenide and Tin Selenide and then composite of Copper Selenide and Indium Selenide to vary the bandgap for its better applications in solar cell.
3. To study the thin films of Copper Selenide, Indium Selenide and Tin Selenide and their composites as follows :

    - Structural properties by X-ray diffraction measurement.
    - Surface morphology study by Scanning Electron Microscopy, Transmission Electron Microscopy, Atomic Force Microscopy.
    - Composition check by X-ray Photoelectron Spectroscopy (XPS) , Raman Spectroscopy ,
    - Fourier-transform Infrared Spectroscopy (FTIR)
    - Optical properties by Ultraviolet-Visible Spectroscopy.
    - Electrical measurement by Four Probe method.

6. RESEARCH METHODOLOGY

6.1 THIN FILM DEPOSITION

Thin Film Deposition can be achieved through two methods: Physical Vapor Deposition (PVD) or Chemical Vapor Deposition (CVD)

Physical Vapor Deposition (PVD) comprises a group of surface coating technologies used for decorative coating, tool coating, and other equipment coating applications. It is fundamentally a vaporization coating process in which the basic mechanism is an atom by atom transfer of material from the solid phase to the vapor phase and back to the solid phase, gradually building a film on the surface to be coated. In the case of reactive deposition, the depositing material reacts with a gaseous environment of co-deposited material to form a film of compound material, such as a nitride, oxide, carbide or carbonitride.

Physical evaporation is one of the oldest methods of depositing metal films. Aluminum, gold and other metals are heated to the point of vaporization, and then evaporate to form to a thin film covering the surface of the substrate. All film deposition takes place under vacuum or very carefully controlled atmosphere.

In the present study , we propose to use thermal evaporation method for preparing thin film.

THERMAL EVAPORATION

Thermal evaporation is the process where the material used for coating is thermally vaporized and then proceeds by potential differences to the substrate with little or no collisions with gas molecules. Normal vacuum levels are in the medium to high vacuum range of 10^{-5} to 10^{-9} mbar. In thermal evaporation techniques, different methods can be applied to heat the material. The equipments available in the laboratory use either resistance heating or bombardment with a high energy electron beam, usually several KeV, from an electron beam gun (electron beam heating) In the Resistance heating technique, the material is heated until fusion by means of an electrical current passing through a filament or metal plate (Evaporator) where the target material is deposited. The evaporated material is then condensed on the substrate.

The other common heat source is an **Electron Beam** or e-beam. The Electron beam heating technique is based in the heat produced by high energy electron beam bombardment on the material to be deposited. The electron beam is generated by an electron gun, which uses the thermionic emission of electrons produced by an incandescent filament. Emitted electrons are accelerated by a high voltage potential . As electrons can be focalized, it is possible to obtain localized heating on the material to evaporate, with a high density of evaporation power. This allows controlling the evaporation rate, from low to very high values, and best of all, the chance of depositing materials with high melting point (W, Ta, C, etc.).

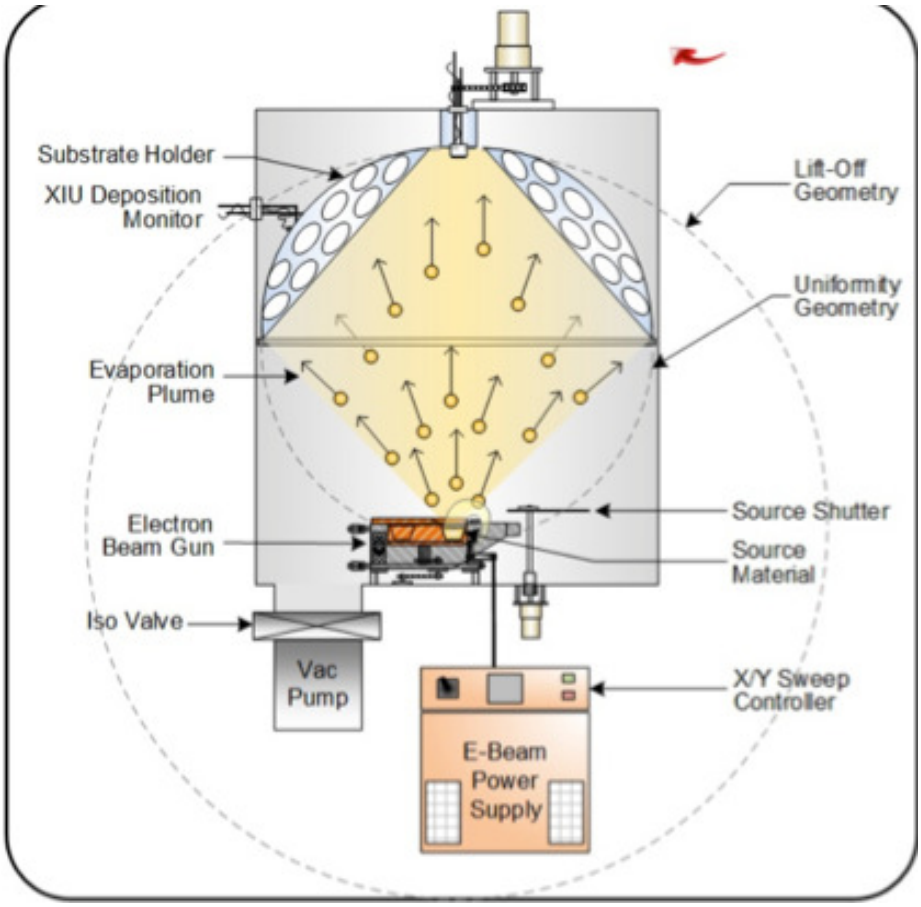


Fig 1: Diagram of Thermal Evaporation Process

6.2 NANOMATERIAL CHARACTERIZATION BY MICROSCOPY:

Optical microscopes are generally used for observing micron level materials with reasonable resolution. Further magnification cannot be achieved through optical microscopes due to aberrations and limit in wavelength of light. Hence, the imaging techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), etc. have been developed to observe the sub micron size materials. Though the principles of all the techniques are different but one common thing is that they produce a highly magnified image of the surface or the bulk of the sample. Nanomaterials can only be observed through these imaging techniques as human eye as well as optical microscope cannot be used to see dimensions at nano level. Basic principles and applications of all these imaging techniques used in nanotechnology research are described below.

6.2.1 SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron microscope is an electron microscope that images the sample surface by scanning it with a high energy beam of electrons. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image while the scanning electron microscope creates the magnified images by using electrons instead of light waves.

Basic Principle

When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, backscattered electrons and characteristic X-rays are generated that contain information about the sample's surface topography, composition, etc . The SEM can produce very high-resolution images of a sample surface, revealing details about 1-5 nm in size in its primary detection mode i.e. secondary electron imaging. Characteristic X-rays are the second most common imaging mode for an SEM. These characteristic X-rays are used to identify the elemental composition of the sample by a technique known as energy dispersive X- ray (EDX). Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample.

In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. Electronic devices are used to detect and amplify the signals and display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope. The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

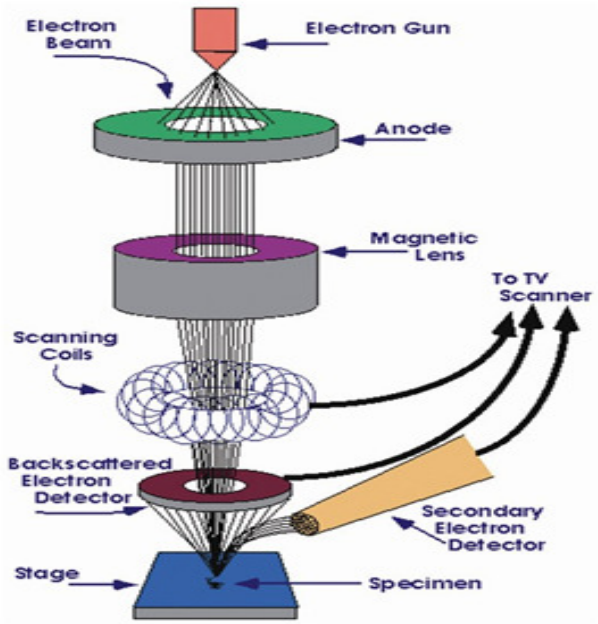


Fig 2: Schematic diagram of SEM

SEM requires that the specimens should be conductive for the electron beam to scan the surface and that the electrons have a path to ground for conventional imaging. Non-conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Non-conducting specimens may also be imaged uncoated using specialized SEM instrumentation such as the "Environmental SEM" (ESEM) or in field emission gun (FEG) SEM operated at low voltage, high vacuum or at low vacuum, high voltage.

6.2.2 ENERGY DISPERSIVE X-RAY ANALYSIS (EDX)

Energy dispersive X-ray analysis is a technique to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample.

Basic Principle

This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20keV. This causes X-rays to be emitted from the material. The energy of the X-rays emitted depends on the material under examination. The X- rays are generated in a region about 2 microns in depth, and thus EDX is not truly a surface science technique. By moving the electron beam across the material an image of each element in the sample can be obtained. Due to the low X-ray intensity, images usually take a number of hours to acquire.

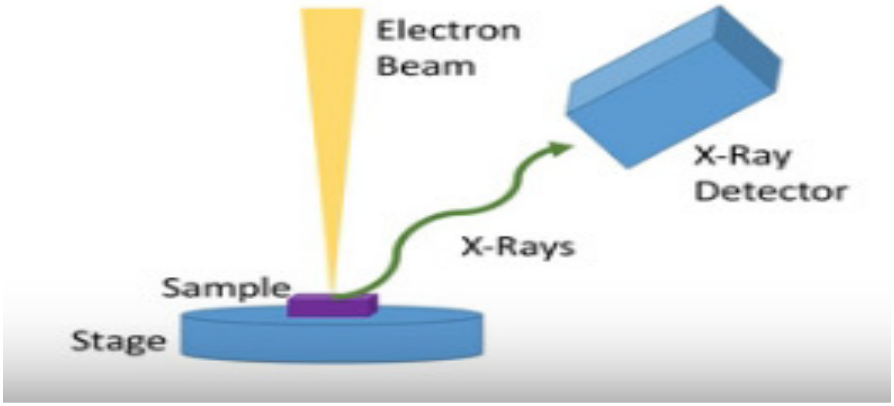


Fig 3 : Schematic diagram of EDX

6.2.3 TRANSMISSION ELECTRON MICROSCOPY (TEM)

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen and interacts as passes through the sample. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen.

Basic Principle

The contrast in a TEM image is not like the contrast in a light microscope image. In TEM, the crystalline sample interacts with the electron beam mostly by diffraction rather than by absorption. The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam; at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted. Modern TEMs are equipped with specimen holders that allow tilting the specimen to a range of angles in order to obtain specific diffraction conditions. Therefore, a high contrast image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through. This produces a variation in the electron intensity that reveals information on the crystal structure. This technique, particularly sensitive to extended crystal lattice defects, is known as 'bright field' or 'light field'. It is also possible to produce an image from electrons deflected by a particular crystal plane which is known as a dark field image.

The TEM is used widely both in material science/metallurgy and biological sciences. In both cases the specimens must be very thin and able to withstand the high vacuum present inside the instrument. For biological specimens, the maximum specimen thickness is roughly 1 micrometer.

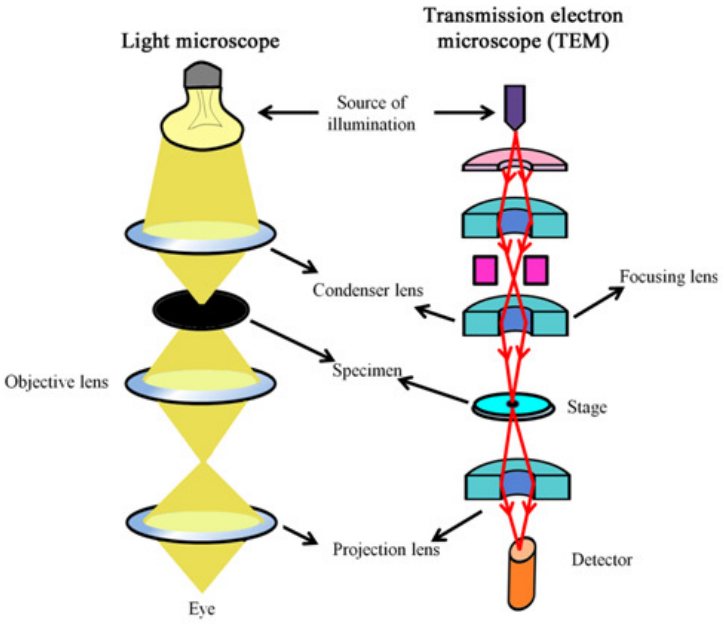


Fig 4 : Schematic diagram of TEM

6.2.4 ATOMIC FORCE MICROSCOPE (AFM)

The atomic force microscope is ideal for quantitatively measuring the nanometer scale surface roughness and for visualizing the surface nano-texture on many types of material surfaces including polymer nanocomposites and nanofinished or nanocoated textiles. Advantages of the AFM for such applications are derived from the fact that the AFM is non- destructive technique and it has a very high three dimensional spatial resolution.

Basic Principle

The basic principle of atomic force microscopy, a probe consisting of a sharp tip (nominal tip radius is in the order of 10 nm) located near the end of a cantilever beam is raster scanned across the surface of a specimen using piezoelectric scanners. Changes in the tip specimen interaction are often monitored using an optical lever detection system, in which a laser is reflected off of the cantilever and onto a position- sensitive photodiode. During scanning, a particular operating parameter is maintained at a constant level, and images are generated through a feedback loop between the optical detection system and the piezoelectric scanners. There are three scan modes for AFM, namely contact mode, non contact mode and tapping mode.

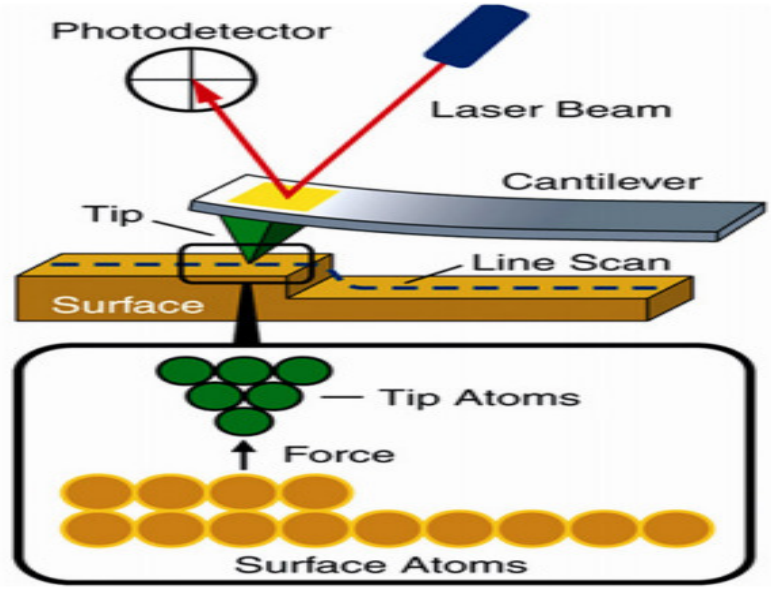


Fig 5 : Schematic diagram of AFM

In contact mode, the tip scans the specimen in close contact with the surface of the material. The repulsive force on the tip is set by pushing the cantilever against the specimen's surface with a piezoelectric positioning element. The deflection of the cantilever is measured and the AFM images are created.

In non- contact mode, the scanning tip hovers about 50–150 Å above the specimen's surface. The attractive forces acting between the tip and the specimen are measured, and topographic images are constructed by scanning the tip above the surface.

Tapping mode imaging is combination of both contact and non-contact mode. When the tip is not in Contact with the surface of a material. The oscillating tip is then moved towards the surface until it Begins to tap the surface.

6.3 NANOMATERIALS CHARACTERIZATION BY SPECTROSCOPY:

6.3.1 RAMAN SPECTROSCOPY

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic laser light. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system.

Basic Principle

The Raman effect occurs when light impinges upon a molecule interacts with the electron cloud of the bonds of that molecule and incident photon excites one of the electrons into a virtual state. For the spontaneous Raman Effect, the molecule will be excited from the ground state to a virtual energy state, and relax into a vibrational excited state, which generates stokes Raman scattering. If the molecule were already in an elevated vibrational energy state, the Raman scattering is then called anti-stokes Raman scattering. A molecular polarizability change or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman Effect. The amount of the polarizability change will determine the Raman scattering intensity, whereas the Raman shift is equal to the vibrational level that is involved.

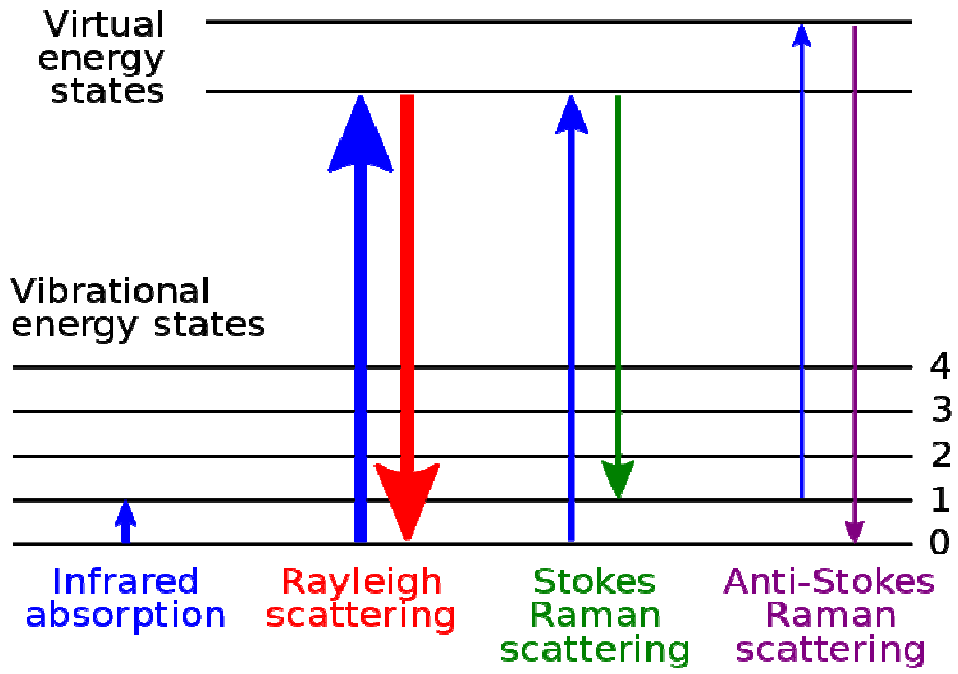


Fig 6: Energy-level diagram showing the states involved in Raman spectra.

6.3.2 ULTRAVIOLET VISIBLE (UV-VIS) SPECTROSCOPY:

Ultraviolet spectrophotometer consist of a light source, reference and sample beams, a Monochromatic and a detector. The ultraviolet spectrum for a compound is obtained by exposing a Sample of the compound to ultraviolet light from a light source, such as a Xenon lamp.

Basic Principle

The reference beam in the spectrophotometer travels from the light source to the detector without interacting with the sample. The sample beam interacts with the sample exposing it to ultraviolet light of continuously changing wavelength. When the emitted wavelength corresponds to the energy level which promotes an electron to a higher molecular orbital, energy is absorbed. The detector records the ratio between reference and sample beam intensities (*Io*/*I*). The computer determines at what wavelength the sample absorbed a large amount of ultraviolet light by scanning for the largest gap between the two beams. When a large gap between intensities is found, where the sample beam intensity is significantly weaker than the reference beam, the computer plots this wavelength as having the highest ultraviolet light absorbance when it prepares the ultraviolet absorbance spectrum.

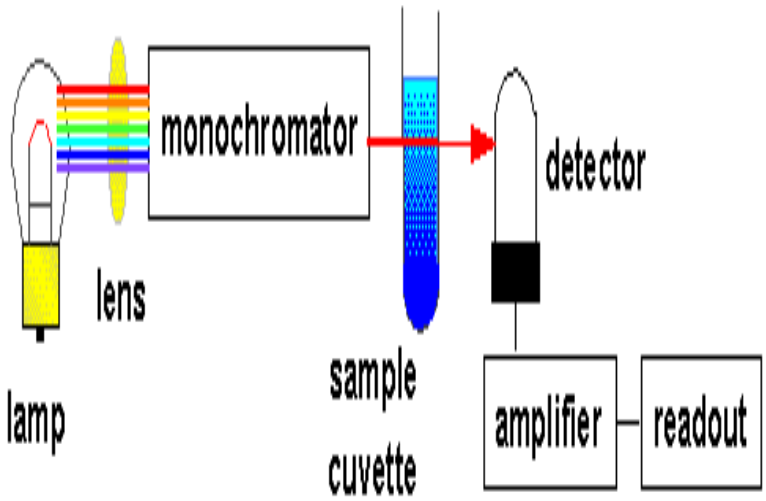


Fig 7: schematic diagram of ultraviolet spectroscopy

6.3.3 X-RAY DIFFRACTION

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength (few Angstrom). They are produced when electrically charged particles of sufficient energy are decelerated. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions.

Basic Principle

If an incident X-ray beam encounters a crystal lattice, general scattering occurs. Although most scattering interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). The relation by which diffraction occurs is known as the Bragg's law. As each crystalline material including the semi crystalline polymers as well as metal and metal oxide nanoparticle and layered silicate nanoclays have a characteristic atomic structure, it will diffract X-rays in a unique characteristic diffraction order or pattern.

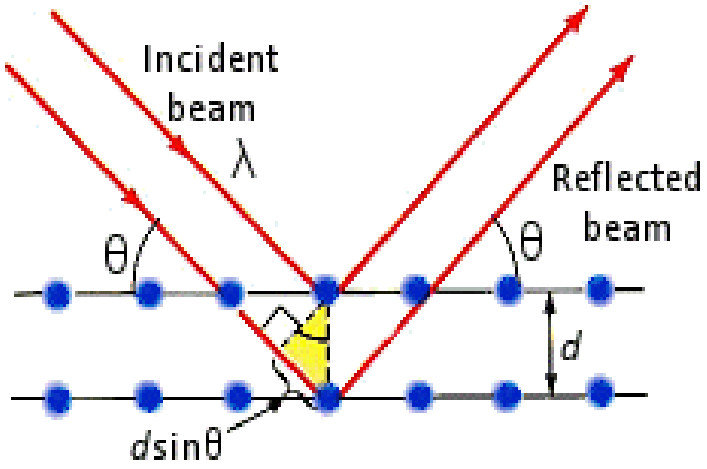


Fig 8 : Schematic diagram of X-Ray diffracion

6.3.4 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

X-ray photoelectron spectroscopy is a quantitative spectroscopic surface chemical analysis technique used to estimate the empirical formula or elemental composition, chemical state and electronic state of the elements on the surface (up to 10 nm) of a material. XPS is also known as ESCA, an abbreviation of electron spectroscopy of chemical analysis.

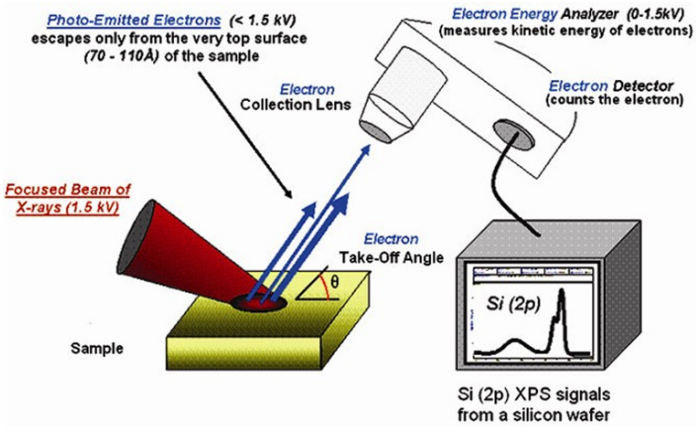


Fig 9: Schematic diagram of X-ray photoelectron spectroscopy

Basic Principle

X-ray irradiation of a material under ultra-high vacuum (UHV) leads to the emission of electrons from the core orbitals of the top 10 nm of the surface elements of the material being analyzed. Measurement of the kinetic energy and the number of electrons escaping from the surface of the material gives the XPS spectra. From the kinetic energy, the binding energy of the electrons to the surface atoms can be calculated. The binding energy of the electrons reflects the oxidation state of the specific surface elements. The number of electrons reflects the proportion of the specific elements on the surface.

As the energy of a particular X-ray wavelength used to excite the electron from a core orbital is a known quantity, we can determine the electron binding energy (BE) of each of the emitted electrons by using the following equation that is based on the work of Ernest Rutherford

$$E_{binding} = E_{photon} - E_{kinetic} - \Phi$$

Where, $E_{binding}$ is the energy of the electron emitted from one electron configuration within the atom; E_{photon}, the energy of the X-ray photons being used ; $E_{kinetic}$ the kinetic energy of the emitted electron as measured by the instrument ;and Φ the work function of the spectrometer (not the material).

6.3.5 FOURIER TRANSFORM ELECTRON SPECTROSCOPY (FTIR)

Fourier Transform Infrared Spectroscopy (FT-IR) is one of the techniques that are used for measuring the intensity of infrared radiation as a function of frequency or wavelength. Infrared radiation is invisible electromagnetic radiation just below the red color of the visible electromagnetic spectrum, with wavelength range from 700 nm to 1 mm

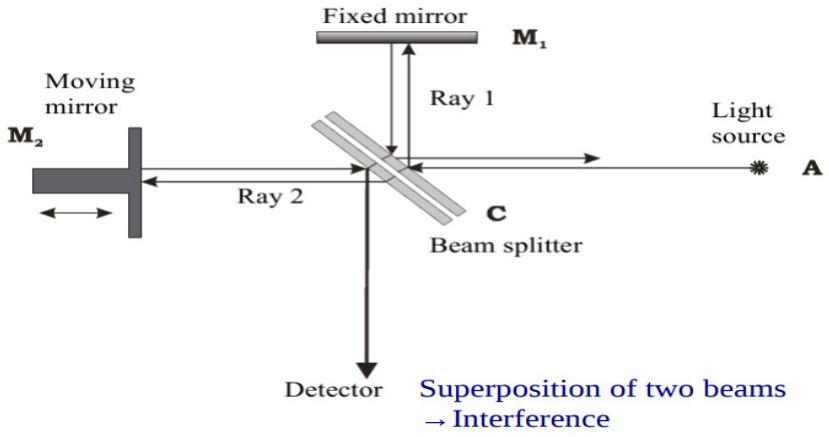


Fig 10 : schematic diagram of Fourier transform electron spectroscopy

Basic principle: An FTIR is typically based on The Michelson Interferometer Experimental Setup: The interferometer consists of a beam splitter, a fixed mirror, and a mirror that translates back and forth, very precisely. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the other half. Radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam splitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source.

6.3.6 FOUR PROBE METHOD

Four Probe method is one of the standard and most commonly used method for the accurate measurement of resistivity. It overcomes the problem of contact resistance and also offer several other advantages. Accurate resistivity measurement in samples having a variety of shapes is possible by this method. The pressure contacts provided in the Four Point Arrangement are especially useful for quick measurement. This setup can measure samples of reasonably wide resistivity range (micro ohm to mega ohm).

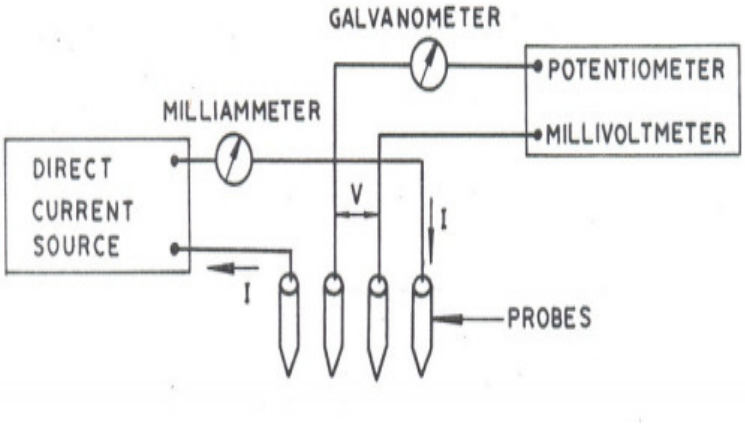


Fig 11: schematic diagram of four probe method

7. RESEARCH WORK PLAN

I. First three months we will do literature survey and then we will learn how to make Thin Film by Thermal Evaporation Technique.

II. Next three months we will deposit Thin film of Copper Selenide, Indium Selenide and Tin Selenide and for another three months we will do characterization by SEM, TEM, XRD, AFM, FTIR, RAMAN ,UV-VIS and XPS. We will prepare research papers to send them for publication and journal at national and international level.

III. Next three months we will deposit composite of Copper Selenide and Tin Selenide and another three months we will do characterization by SEM, TEM, XRD, AFM, FTIR , RAMAN, UV-VIS and XPS. We will prepare research papers to send them for publication in conferences.

IV. Next three months we will deposit composite of Copper Selenide and Indium Selenide and another three months we will do characterization by SEM, TEM, XRD, AFM, FTIR ,RAMAN, UV-VIS and XPS.

V. Next three months we will prepare research papers to send them for publication and journal at national and international level.

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